



## Determination of thallium at ultra-trace levels in water and biological samples using solid phase spectrophotometry

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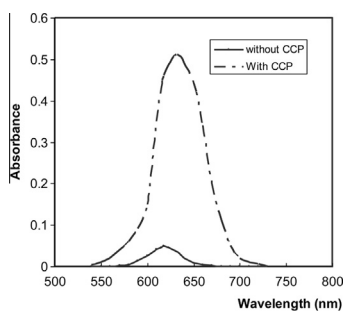
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### HIGHLIGHTS

- ▶ Sensitive procedure to determine trace amounts of Tl(III) by SPS has been developed.
- ▶ The procedure is based on fixation of Tl(III) as ion associate on anion-exchange resin.
- ▶ The absorbance of resin sorbed Tl(III) ion associate is measured directly at 636 and 830 nm.
- ▶ The procedure has been successfully applied to determine Tl(III) in real samples.

### GRAPHICAL ABSTRACT

The procedure is based on fixation of Tl(III) as quinalizarin ion associate on a styrene–divinylbenzene anion-exchange resin. The absorbance of resin sorbed Tl(III) ion associate is measured directly at 636 and 830 nm. Thallium(I) was determined by difference measurements after oxidation of Tl(I) to Tl(III) with bromine. Calibration is linear over the range 0.5–12.0  $\mu\text{g L}^{-1}$  of Tl(III) with relative standard deviation (RSD) of 1.40% ( $n = 10$ ). The detection and quantification limits are 150 and 495  $\text{ng L}^{-1}$  using 0.6 g of the exchanger. The proposed procedure has been successfully applied to determine thallium in water, urine and serum samples.



Absorption spectra for 8.0  $\mu\text{g L}^{-1}$  Tl(III) complexed with 5.6  $\times 10^{-6}$  M QZL 1- without CCP and 2- with CCP

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### ABSTRACT

A new simple, very sensitive, selective and accurate procedure for the determination of trace amounts of thallium(III) by solid-phase spectrophotometry (SPS) has been developed. The procedure is based on fixation of Tl(III) as quinalizarin ion associate on a styrene–divinylbenzene anion-exchange resin. The absorbance of resin sorbed Tl(III) ion associate is measured directly at 636 and 830 nm. Thallium(I) was determined by difference measurements after oxidation of Tl(I) to Tl(III) with bromine. Calibration is linear over the range 0.5–12.0  $\mu\text{g L}^{-1}$  of Tl(III) with relative standard deviation (RSD) of 1.40% ( $n = 10$ ). The detection and quantification limits are 150 and 495  $\text{ng L}^{-1}$  using 0.6 g of the exchanger. The molar absorptivity and Sandell sensitivity are also calculated and found to be  $1.31 \times 10^7 \text{ L mol}^{-1} \text{ cm}^{-1}$  and 0.00156  $\text{ng cm}^{-2}$ , respectively. The proposed procedure has been successfully applied to determine thallium in water, urine and serum samples.

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## Introduction

Thallium (Tl) is a non-essential toxic element with no known beneficial biological role, which has various industrial applications [1–5] such as semiconductors, nuclear medicine, catalysts, dyes and pigments; thereby increasing the risk of occupational poisoning and environmental pollution. It is known that Tl is more toxic than Hg, Pb, Cu and Cd [6,7]. Water is probably the most studied environmental sample and in fact the major part of Tl studies has been carried out in waters. But as the concentration of Tl in natural waters is below  $\text{ng L}^{-1}$  level [8–11] the development of new methods for selective separation, preconcentration, purification and determination of this metal continues to be a challenging problem.

The monitoring of aquatic environment for Tl and its speciation have drawn the attention of researchers due to its high toxicity [12–16]. Tl in bottled water was determined by inductively coupled plasma-mass spectrometry (ICP-MS) [13,14] and Tl in arctic snow and seawater was determined by electrothermal vaporization ICP-MS [17] and flow-injection hydride generation isotope dilution ICP-MS [18], respectively. Laser-excited atomic fluorescence spectrometry (LEAFS) is also highly sensitive to Tl and used for the analysis of snowmelt [19]. However, ICP-MS needs expensive instrumentation and incurs high running cost, and LEAFS is less frequently used.

Numerous methods have been proposed for the spectrophotometric determination of Tl [20–23], most of which are based on extraction of ion-associates formed by basic dyes and Tl. These methods, however, are time consuming, have poor selectivity and also have the disadvantage of high blank values. Some of the other chromogenic reagents proposed for the determination of Tl are iodoacetic acid and hexamethylenetetramine [24], pyronine G [25], brilliant green [26,27], mepazine hydrochloride [28], bromopyrogallol red [29], the azo compounds of benzimidazole [30], alizarin violet [31], and phenosafranin [32]. Although the methods involving these reagents are sensitive, they lack selectivity and suffer from serious interference of foreign ions normally occurring in the determination of Tl(III). Other notable methods used for the determination of Tl include ICP-MS [33–37], atomic absorption spectroscopy (AAS) [38–41], X-ray fluorescence [42], electroanalytical methods [43–49] and spectrometry [50–52]. Most of these methods are disadvantageous in terms of cost and instruments used in routine analysis. AAS is often lacking in sensitivity and is affected by the matrix conditions of samples such as salinity. Hence, accurate determination of Tl at trace levels using a simple and rapid method is of paramount importance. Spectrophotometric methods can be used for the determination of trace amounts of Tl occurring in many samples. The availability of the spectrophotometric apparatus and the simplicity of analytical procedures make the technique very attractive for a wide range of applications. A recent literature survey also revealed that there is no report of effective and sensitive spectrophotometric methods for Tl(I) and Tl(III). These deficiencies encouraged the authors to develop a simple, rapid, inexpensive and reliable method for the determination of trace amounts of total Tl in various samples.

Many separation and preconcentration techniques for the determination of Tl and other metals have been proposed including solvent extraction [53–56], co-precipitation [57], high performance liquid chromatography [58], ion exchange chromatography [59] and solid phase extraction [60–64]. However the conventional solvent extraction and co-precipitation are laborious and are apt to carry a risk of contamination. Of all above methods, solid phase extraction has attracted great attention owing to its simple operation, rapid phase separation emulsification, highly enrichment factor and easily automation.

Solid-phase spectrophotometry (SPS) is a technique based on the preconcentration of the substance in question on a solid, aided by complexing (or other reagents), and the subsequent measurement of the absorbance of the species in the solid phase. This provides SPS with an increase in selectivity and sensitivity over other methods [65–71]. Thus, detection limits as low as  $0.10 \mu\text{g L}^{-1}$  have been reported. The goal of the present work is intended to study the possibilities of using quinalizarin as a reagent for the determination of trace Tl(III) by SPS. The optimum conditions have been established. Tl(III) reacts with quinalizarin to give a colored ion associate complex, which is easily sorbed on an anion-exchange resin and provides the basis for a relatively simple, accurate and rapid spectrophotometric method of Tl(III) at  $\mu\text{g L}^{-1}$  level, without a previous preconcentration step. The proposed method is free from many interferences and has been applied to the determination of Tl(III) in tap, mineral, well water and in biological samples.

## Experimental

### Apparatus

A Perkin Elmer Lambda 12 UV-vis spectrophotometer with a 5.0 mm quartz cell was used for all spectral measurements. An Orion research model 601A/digital ionalyzer pH meter was used for checking the pH of buffer solutions of pH values ranging from 2.5 to 12.0, prepared as recommended previously [72].

### Reagent

Analytical reagent grade chemicals and doubly distilled water were used throughout. An appropriate weight of quinalizarin (QLZ) was dissolved in 100 ml of absolute ethanol to prepare  $10^{-3} \text{ M}$  in a 100 ml measuring flask.

Tl(I) and (III) stock solution both  $1000 \mu\text{g ml}^{-1}$  was prepared by dissolving an appropriate weight of thallos nitrate (99.99%) and thallic nitrate (99.999%), from Riedel de Haen, in 2.0% nitric acid, and the desired concentration was attained by proper dilution.

Styrene divinylbenzene anion exchange resin (commercial trademark) was used in the chloride form. The resin was soaked in alcohol for 12.0 h, then treated with 2.0 M HCl for 6.0 h, finally with distilled water until the washing was free from chloride. It was dried at  $40^\circ\text{C}$  and stored in a brown reagent bottle.

### Absorbance measurements

The absorbance of QLZ-Tl(III) ion associate sorbed on the resin was measured in a 5.0 mm cell at 636 and 830 nm against a 5.0 mm cell packed with resin equilibrated with blank solution. The net absorbance ( $A_c$ ) for the ion associate was obtained using the equation [68,70]:

$$A_c = A_{636} - A_{830}$$

where  $A_{636} = A_{s, 636} - A_{b, 636}$  and  $A_{830} = A_{s, 830} - A_{b, 830}$  and  $A_{s, xxx}$  and  $A_{b, xxx}$  are the absorbances of the sample and the blank (cell packed with resin equilibrated with blank solution), respectively at the indicated wavelength. When the absorbance was measured at two different wavelengths, one corresponding to absorption maximum of the ion associate (636 nm) and the other in a region where the ion associate absorbs very low (830 nm), the absorbance difference,  $A_{636} - A_{830}$ , could be assumed to be constant under the similar packing conditions.

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